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IMPROVE THE THERMAL SHOCK RESISTANCE OF ZIRCONIA

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INVESTIGATION OF THE MECHANISM BY WHICH METAL ADDITIONS IMPROVE
THE THERMAL SHOCK RESISTANCE OF ZIRCONIA

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ABSTRACT

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In this investigation, the relatively good thermal shock resistance of zirconia with 15 mole percent titanium for quenches from below the transformation temperature of zirconia was traced to the presence of metal in the grain boundaries. The discrepancy between calculated and experimental thermal shock resistance of the same compositions for quenches through the transformation range was traced to the plastic behavior of these materials through the transformation range. The same type of plasticity was observed through the transformation range of zirconia-zirconium compositions. Many other metals besides titanium improved the thermal shock resistance of zirconia.

Author

SUMMARY

The shape of the cracks of thermally shocked disks and bent modulus of elasticity specimens indicated that the discrepancy between the experimental and calculated thermal shock resistance of zirconia with 15 mole percent titanium for quenches through the transformation range might be due to plasticity. An investigation of this property showed that zirconia with 15 mole percent titanium deforms plastically on heating and cooling through the transformation range of zirconia. Zirconia-zirconium cermets were shown to behave in a similar manner. Due to the possibility that this plastic behavior involves grain boundary sliding,

[Redacted]

the nature of the grain boundaries in zirconia with 15 mole percent titanium was investigated.

Experiments indicate that the grain boundaries in zirconia with 15 mole percent titanium contain patches of a metallic phase that would allow grain boundary displacements without fracture. Incidental to this part of the investigation it is shown that the black color of the zirconia-titanium compositions is due to the presence of metal in them.

Thermal shock experiments with other zirconia-metal compositions show that titanium is by no means unique in its ability to improve the thermal shock resistance of zirconia.

It is surmised that the results of this investigation are applicable - at most with minor changes - to hafnia and thoria, and that the thermal shock resistance of other ceramics can be improved by metal additions.

I. INTRODUCTION

In a previous investigation¹ it has been found that the good thermal shock resistance of zirconia with 15 mole percent titanium for quenches from below the transformation temperature of zirconia can be explained on the basis of the smaller grain size - and hence higher strength - of these compositions compared with that of calcia-stabilized zirconia. For this reason, experiments to determine the effect of titanium on grain growth were carried out.

On the other hand, it has been shown in a previous report² that the discrepancy between the experimental and the calculated thermal shock resistance of milled zirconia with 15 mole percent titanium for

quenches through its transformation range cannot be explained solely from the values of the material properties that appear in the thermal shock equation alone and some other explanation must be sought. Certain experimental observations indicate that this improvement in thermal shock resistance may be due to the plasticity of the material.

During the determination of the modulus of elasticity of zirconia with 15 mole percent titanium,² some of the bars showed a slight permanent curvature after testing, and it will be shown in this paper that zirconia with 15 mole percent titanium disks cracked by thermally shocking them through the transformation range have open cracks. In addition, it has been reported³ that zirconia with 15 mole percent titanium compositions exhibited plasticity at room temperature, but no evidence of such behavior was noted in the room-temperature modulus-of-elasticity and modulus-of-rupture determinations for the zirconia with 15 mole percent titanium compositions used in this investigation. For this reason, experiments were carried out to determine the lowest temperature at which plastic deformation could be observed in the zirconia-titanium material used in this investigation.

Other experiments carried out in this investigation are intended to show the effects of other metal additions on the thermal shock resistance of zirconia.

III. MATERIALS AND SPECIMEN PREPARATION

RAW MATERIALS

A list of the raw materials used in this investigation together with supplier's designations, typical chemical analysis, original particle size, and method of particle size determination are given in Table 1.

SPECIMEN PREPARATION

Prismatic bar and disk specimens of the various compositions to be designated were prepared by standard powder-metallurgy techniques. Specimen designations, composition, and method of preparation are summarized in Table 2.

The designations used are intended to convey, in a group of letters and numbers, the composition and method preparation. The first letter in the group indicates the matrix oxide (Z for zirconia, H for hafnia, B for stabilized zirconia). The second letter designates the addition (T for titanium, Z for zirconium, etc.). The number following these letters indicates the mole percent metal addition. The last letter or group of letters indicates the method of preparation (M for milled, HP for hot-pressed, and mixed if there is no letter following the mole percent addition).

In the compositions designated as mixed in Table 2, the previously dried and weighed raw materials were mixed in cone blenders, 5 weight percent water added as a temporary binder, cold-pressed into shape in steel dies, hydrostatically cold-pressed at 46,000 to 50,000 psi in evacuated plastic tubing, dried in a vacuum desiccator, and vacuum-sintered at $1870 \pm 30^\circ \text{ C}$ for 1 hour.

In the compositions designated as milled, the previously dried and weighed raw materials were milled in 2 liter-capacity tungsten carbide mills with tungsten carbide balls and a liter of acetone as the grinding media for 72 hours at 80 rpm. After milling, the acetone was removed by evaporation in a stream of warm air, the powders were mixed

with 5 weight percent water as a temporary binder, and the specimens were prepared as outlined for the mixed compositions, except for the compositions designated as BM, which were sintered at 1800° C for 3 hours in air.

The compositions designated as hot-pressed were prepared by mixing the previously dried and weighed raw materials followed by vacuum hot-pressing in graphite dies at the temperatures and times indicated in Table 2.

All the specimens were ground all over with diamond wheels to a finish of 50 microinches or better and the surface-ground specimens were inspected for cracks and pin holes by means of dye penetrant.

Some experiments were carried out for which the specimens were prepared by procedures different from those outlined. These specimens have no special designation.

The milling, sintering, and hot-pressing equipment used has been thoroughly described in reference 4.

III. EXPERIMENTAL PROCEDURES AND RESULTS

EFFECT OF TITANIUM ADDITIONS ON GRAIN GROWTH OF ZIRCONIA

As already stated, the good thermal shock resistance of the zirconia-titanium compositions for quenches from below their transformation range can be explained (at least in part) on the basis of their smaller grain size compared with that of calcia-stabilized zirconia. This grain size difference may be due to inherent properties of the matrix materials, to the effect of calcia on the grain growth of zirconia, or to the effect of titanium in inhibiting the grain growth of zirconia. For this reason, experiments to determine the effect of titanium on grain growth were carried out.

Small specimens of pure zirconia (CP Zirox, Table 1) were cold-pressed and vacuum-sintered by the same techniques used for the ZT-15 zirconia-titanium composition. The microstructure of the vacuum-sintered pure zirconia is shown in Fig. 1(a) where the black or dark gray areas are pores. Despite the fact that pure zirconia was sintered at a slightly lower temperature, its grain size is about five times that of zirconia with 15 mole percent titanium (ZT-15), as comparison of Figs. 1(a) and 2 will show. It is concluded from this experiment that the titanium additions inhibit the grain growth of zirconia and thereby increase its strength.

ELASTOPLASTIC PHENOMENA ON HEATING AND COOLING

THROUGH TRANSFORMATION RANGE

In reference 1, disks of zirconia with 15 mole percent titanium as well as disks of calcia-stabilized zirconia were thermally shocked both from below and from above the transformation temperature of the zirconia in the former compositions. Typical thermally shocked disks of both compositions are shown in Fig. 3. It should be noted that disks of ZT-15-M thermally shocked from below the transformation temperature usually crack only part way and have closed cracks (Fig. 3(a)) as contrasted with disks of the same material thermally shocked from above the transformation range of zirconia which also crack part way but exhibit open cracks (Fig. 3(c)). Thermally shocked calcia-stabilized zirconia, on the other hand, always cracks all the way through, and the two parts match perfectly (Fig. 3(b)). The results of these experiments indicate first that the titanium addition tends to arrest crack propagation and second that specimens of zirconia

with 15 mole percent titanium deform plastically when cooled through the transformation range.

As already mentioned in the INTRODUCTION, some of the modulus-of-elasticity bars made from milled zirconia with 15 mole percent titanium (ZT-15-M) used in reference 2 showed a slight permanent curvature after testing. Room-temperature ductility on this type of material has been reported previously in the literature.³ In order to determine the extent of the assumed plastic deformation and the temperature at which it takes place, additional experiments were carried out.

These experiments were performed in the semiautomatic modulus-of-rupture tester and high-temperature vacuum testing furnace described in reference 5. This modulus-of-rupture tester is of the three-point-loading type, and bar specimens can be heated or cooled in vacuum under constant load. The loads are applied with a tensile machine and the total cross-head motion can be accurately monitored with a deflectometer that allows determination of the deflection of the specimen. This is done by subtracting the furnace deformation under the same load (obtained by using a thick bar of tungsten as modulus-of-rupture specimen) from the total deformation when testing with a thin bar of a material whose deflection is sought. As explained in reference 5, a number of specimens can be positioned under the push rod for loading or removed from the loading position at any time during the run.

The plastic deformation of milled zirconia with 15 mole percent titanium (ZT-15-M) was determined on prismatic bar specimens 2.35 inches long by 0.50 inch wide by 0.100 to 0.125 inch high. A specimen of ZT-15-M (to be designated as specimen A) was heated in the tester at a

rate between 3° and 5° C per minute (in vacuum) under a constant stress of about 50 percent of its room-temperature rupture stress.² Constant recordings of the deflections at this constant stress were taken and the readings corrected for furnace plus tester deformation at each temperature. At the end of the run (at about 1150° C) specimen A was removed from the loading position and a new specimen B (kept in the magazine of the tester during the heating cycle) was placed in the loading position. This specimen B was also loaded to about 50 percent of its room-temperature rupture stress and cooled at a rate between 3° and 5° C per minute, while taking continuous recordings of the deflections, which were also corrected for furnace plus tester deformation as indicated above. The corrected deflection-temperature curves for both specimens are shown in Fig. 4, which also includes a thermal-expansion - temperature curve for the same kind of material² to show the relation between transformation temperature and plastic deformation. As a comparison of the curves in Fig. 4 shows, deformation of the loaded specimens both on heating and cooling starts when transformation starts and ends when transformation ends.

Figure 5 shows these specimens of ZT-15-M after the experiments just described. The curvature of the specimens corresponds to the maximum deflections, both on heating and on cooling, shown for the modulus-of-rupture specimens in Fig. 4. It should be noted that specimen A straightened itself out on heating above 1100° C, as shown in Fig. 4, and consequently it must have bent by itself on cooling. Experiments with other specimens showed that this return to the bent position takes place on cooling (without load) through the transformation temperature.

The approximate amounts of plastic deformation involved in these experiments can be determined on the assumption that the curvature of the specimens shown in Fig. 5 can be approximated by that of circular arcs of radius r

$$r = \frac{L^2}{\delta}$$

where L is the span between the rods of the modulus-of-rupture tester (2.000 in.), and δ is the deflection (sagitta) at the midspan of the bar. Letting d be the thickness of the bent bar ($d = 0.100$ in. for both specimens in Fig. 5) gives the elongation of the bottom fibers per unit length $\Delta L/L$ with respect to the neutral axis of the bar:

$$\frac{\Delta L}{L} = \frac{4d\delta}{L^2}$$

With $\delta = 0.082$ inch (from Fig. 4)

$$\frac{\Delta L}{L} = \frac{4 \times 0.100 \times 0.082}{4} = 0.0082 \text{ in./in.}$$

or 0.82 percent plastic deformation for ZT-15-M at rupture during cooling.

In order to determine whether the plastic deformation was an intrinsic property of the zirconia matrix and not plasticity brought about by a modification of the transformation mechanism caused by the presence of titanium ions in the zirconia structure, plastic deformation experiments with vacuum hot-pressed zirconia (Z-0-HP) were carried out. This vacuum hot-pressed zirconia is actually a cermet of zirconia and (oxygen saturated) zirconium metal, as shown in the photomicrograph of Fig. 6.

The experiments with the vacuum hot-pressed zirconia were similar to those carried out with ZT-15-M. The deflection-temperature curves for Z-0-HP are shown in Fig. 7. The corresponding bent specimens are

similar to those of ZT-15-M shown in Fig. 5. The specimen of Z-O-HP (designated as specimen C in Fig. 7) used for the heating cycle fractured so that it is not certain whether this material would have straightened itself out on continued heating. The specimen of Z-O-HP (designated as specimen D in Fig. 7) used for the cooling cycle deformed just like that of ZT-15-M composition but underwent up to 1.11 percent outer fiber deformation without breaking. The transformation temperature of the Z-O-HP type of material was determined with the dilatometer described in reference 4 and was about 80°C higher than that of ZT-15-M. The relation between plastic deformation and transformation temperature in Z-O-HP was practically the same as that for ZT-15-M.

The low-temperature ductility of zirconia-titanium compositions reported in reference 3 could not be substantiated by the preceding and similar, low-temperature experiments.

The elastoplastic behavior through the transformation range of zirconia described in the previous paragraphs accounts for the discrepancy between the experimental and calculated ΔT for quenches through the transformation range of zirconia described in reference 2. As can be ascertained from the thermal shock equation,² an increase in the strength $\sigma_{\theta_{\max}}$, or a decrease in the modulus of elasticity E , of the material will decrease ΔT . According to Griffith's theory, the low tensile strength of ceramics compared with their compressive strength is due to the stress-raising effects of cracks, and plasticity can be expected to increase $\sigma_{\theta_{\max}}$ by relieving stress concentrations. On the other hand, the effects of plasticity could be introduced into the

thermal shock equation by using a stress dependent modulus of elasticity. This elastoplastic modulus would be lower than the purely elastic modulus, in the presence of plasticity. Thus, the net effect of plasticity would be to raise ΔT . This elastoplastic behavior also accounts for the difference in the shape of the cracks developed on thermally shocking the specimens from below and through the transformation range, and for the bending of modulus-of-elasticity specimens.

The plastic deformation described appears to be a function of temperature, load, specimen size, and so forth, but a complete study of these variables was beyond the scope of this investigation.

To the writer's knowledge, this is the first time that such a plastic behavior through the transformation range of a ceramic has been observed, but this phenomenon is not new in the case of metals. Plastic deformation during the martensitic transformation of gold-cadmium single crystals has been described.⁶ Similar phenomena have been reported for the martensitic transformation in the indium-thallium system,^{7,8} for the martensitic transformation in iron alloys,⁹ and so forth. The plasticity in some of these alloys has been shown to be caused by twinning of one of the phases followed by the movement of the twinning plane under the influence of a shear stress. In some of these alloy systems the twinned phase is a tetragonal phase. On the other hand, natural monoclinic zirconia is known to twin,¹⁰ and the possibility exists that the plasticity is due to the movement of either a monoclinic or tetragonal twin interface or of both.

Considering that the transformation temperature of zirconia is stress dependent¹¹ the plastic deformation could also be explained,

in part, by this effect, at least qualitatively. Thus, on heating a test bar, the applied stress would reduce the transformation temperature of the top fibers in the test bar causing them to shrink faster than the bottom fibers at first. Eventually, the bottom fibers would also transform causing the bar to straighten itself out. This mechanism, however, does not explain why the bar does not straighten itself out after transformation is completed when the specimen is bent on cooling.

The similarity of behavior between the zirconia-titanium (ZT-15-M) or zirconia-zirconium (Z-O-HP) compositions and martensitic alloys as well as the fact that the transformation can be arrested by holding the temperature constant (as noted in connection with the thermal expansion of ZT-15-M in Ref. 2) suggest that the zirconia in these compositions transforms martensitically rather than by nucleation and growth, but further work would be required to clarify this point.

NATURE OF GRAIN BOUNDARY IN ZIRCONIA WITH 15 MOLE PERCENT TITANIUM

Whatever the transformation mechanism of zirconia may be, atoms are displaced during the transformation with a concomitant volume change in the material. If a grain transforms, it and the adjacent grains will be under stress, and the grain will transform in such a way as to minimize this stress. The movement of these grains must involve a rather large amount of grain boundary sliding. For this reason, experiments were carried out in order to establish the nature of the grain boundaries in the zirconia-titanium compositions.

Milling and Sintering Experiments

Milled zirconia with 15 mole percent titanium is dark gray, while the same mixed composition is light gray, and pure zirconia is white. This suggests that color depends on the degree of dispersion of the metal. Pellets of these three compositions were individually vacuum-sintered at successively higher temperatures up to the melting point. The specimens were polished and examined under the microscope.

Whereas the melting point of pure zirconia has been reported to be about 2700° C, the (zirconium-rich) vacuum-sintered material melted at temperatures below 2620° C. Zirconia with 15 mole percent titanium, on the other hand, was observed to melt at about 2400° C. This lowering of the melting point was to be expected in view of the published zirconia-oxygen phase diagrams.¹²⁻¹⁴ It appears from these experiments that titanium additions lower the melting point of zirconia just as excess zirconium does, although not necessarily in the same amount.

Pure vacuum-sintered zirconia was observed to change from white to a yellowish light gray after sintering runs up to about 2150° C, at which temperature the sintered pellets were black. The change from white to light gray during sintering runs below about 2150° C is attributed to zirconium metal precipitating out on cooling through the 1580° C range, according to the zirconium-oxygen phase diagram of reference 14. Microstructures for the vacuum-sintered pure zirconia are shown in Fig. 1. The grain boundaries of the pellet sintered at 2400° C contain oxygen-saturated zirconium metal (according to the phase diagram of Ref. 14). No metal is visible in the specimens sintered at 1980° C and below. It is quite probable that the boundary metal forms on cooling through the

solidus line in the phase diagram (Ref. 14). Thus, the black color of these compositions appears to be due to the metal in the grain boundaries. The microstructure of vacuum-melted originally pure zirconium oxide is shown in Fig. 1(d). This structure shows zirconium metal in the grain boundaries and a precipitate of lamellar zirconium, which resembles pearlite in structure.

The mixed zirconia with 15 mole percent titanium (equivalent to ZT-15, except for sintering temperature) darkened gradually as the sintering temperature was increased and became black in the range 1400° to 1600° C. The milled zirconia with 15 mole percent titanium (equivalent to ZT-15-M, except for sintering temperature) became black on sintering below 1000° C for 1 hour. Up to sintering temperatures near 2200° C, the microstructures of these compositions are similar to that shown in Fig. 2, except for gradually increasing grain size.

Similar sintering experiments showed nickel metal to blacken zirconia, and titanium to blacken alumina and magnesia on vacuum-sintering the ceramic-metal-powder compacts in the range 1000° to 1600° C for 1 hour. It seems quite probable from these experiments that the black color of the zirconia-titanium compositions is not due to nonstoichiometry. The black color of these compositions probably is due either to the solubility of titanium in zirconia or to a coating of metallic titanium on the zirconia particles.

According to the work reported in reference 15, titanium dissolves substitutionally in zirconia, but the fact that the material becomes dark at such low temperatures and dark gray on milling at room temperature precludes the possibility that the dark color is due to the tita-

nium solubility in zirconium oxide, as this would require very large diffusion coefficients. Further, if titanium dissolves substitutionally in zirconia, the resulting structure would be equivalent to that obtained by mixing corresponding amounts of titania and zirconia.

For low amounts of titania, these two oxides probably form a solid solution,¹⁶ and there is no reason to believe that its properties would be much different from those of zirconia. Consequently, and also in light of the plasticity obtained in the present investigation, the assumption of reference 15 that the good thermal shock resistance of the zirconia-titanium compositions is due to the solubility of titanium in zirconia is questionable.

In order to test the second possibility, that is, that the black color of the material is due to coating of the particles, a series of tests were carried out.

Electron Photomicrographs

An electron photomicrograph of deeply etched ZT-15-M is shown in Fig. 8. The replica material pulled out of the grain boundaries suggests the presence of a different phase there.

Etching Experiments

Approximately 1-gram samples of the two types of zirconia with 15 mole percent titanium (i.e., the "mixed" and the "milled" types) were sintered at various temperatures in vacuum, crushed, and then finely ground in a tungsten carbide mortar and pestle. These samples were digested for 24 hours in a hot, strong acid (sulfuric, hydrochloric, or phosphoric appear to give about the same results). The acid slowly attacked the samples, which became lighter in color with increasing

reaction time. The samples that had been sintered at low temperatures ($< 1500^{\circ}$ C) became a very light gray, whereas the samples that had been sintered at high temperatures became a darker gray. This showed that the black color of the samples was due to the presence of a distinct phase at the grain boundary, probably a titanium-zirconium-oxygen alloy. The gray color remaining after etching is attributed to trapped metallic particles or to patches of the dark grain boundary surrounded by a normal zirconia-zirconia grain boundary, since, as shown in Fig. 8, the grain boundary phase may be discontinuous. This explains why this kind of material can retain a certain amount of strength even above the melting point of the metallic phase.²

Low-Temperature Sintering Experiments

Pellets made from the "mixed" and from the "milled" varieties of zirconia with 15 mole percent titanium were vacuum-sintered at 1000° C for 1 hour. The former was gray and the latter black. Microscopic examination showed that in the former, the material immediately surrounding the metallic particles was dark and could be polished, whereas the material away from the metallic particles was lighter in color and was eroded away by the polishing operation. The pellet made by sintering the "milled" material was uniformly dark in color and polished evenly. The more uniform structure of the latter composition is attributed to the more rapid rate of coating of titanium on the zirconia particles due to the smaller particle size and greater degree of dispersion of the titanium in the "milled" composition. From the results of the preceding series of experiments, it was reasonable to conclude that the black color of the material was due to titanium (not necessarily pure

or continuous) in the grain boundaries, since zirconia is known to be translucent.¹⁷

It can also be surmised from the results of the preceding experiments that the titanium can cause grain growth inhibition by presenting an obstacle to the movement of the grain boundaries.¹⁸ It appears that, in addition to initial particle size, final sintering temperature, time at temperature, and amount of titanium, the properties of the material will also depend on the heating rate, since all these factors will determine the amount of titanium coated or reacted in the would-be grain boundaries.

A metallic grain boundary, such as the one formed in the zirconia-titanium or zirconia-zirconium compositions, in addition to helping arrest crack propagation, can be expected to allow grain boundary sliding because of the ductility of the metallic phase even if saturated with oxygen. On the other hand, the small grain size of the zirconia-titanium compositions (compare Figs. 1(a) and 2(b)) means a large specific grain boundary area and correspondingly smaller relative grain displacements to accomodate a given plastic strain. Large grains, such as those shown in Figs. 1(c), 1(d), and 6, require correspondingly thicker metallic grain boundaries in order to prevent cracking on cooling through the transformation temperature. It should be pointed out that, for the small grain size of Fig. 2(b), the metallic grain boundary would be too thin to be visible in the light microscope even if all the metal were in the grain boundary (which obviously is not, from Fig. 2(a)).

THERMAL SHOCK RESISTANCE OF ZIRCONIA
WITH OTHER METAL ADDITIONS

If the thermal shock resistance of zirconia is due to the presence of metal in the grain boundary, there should be other metals besides titanium capable of improving the thermal shock resistance of zirconia (or of other ceramics, for that matter).

In order to determine whether or not other metals have the same effect as titanium in improving the thermal shock resistance of zirconia, compositions of zirconia with 15 mole percent metallic additions were made by milling, cold-pressing, and sintering, as indicated under MATERIALS AND SPECIMEN PREPARATION and in Table 2. The additions were zirconium, chromium, vanadium, silicon, tungsten, and molybdenum. A sample of hafnia with 15 mole percent titanium was made in the same manner. The designations of these compositions are shown in Table 2.

Zirconia bodies containing tungsten, molybdenum, and silicon could not be made without severe cracking. The samples made with tungsten or molybdenum invariably cracked despite very slow cooling rates. These samples were metallic dark gray probably reflecting the color of the metal powder, since, as already stated, zirconia is translucent.¹⁷ The disks containing silicon also cracked even under very slow cooling rates. The disks had a light gray center tapering off to the light yellowish-gray of vacuum-sintered pure zirconia at the edges. Microscopic examination showed that the gray center contained silicon particles with none at the edges of the disk. This effect is attributed to the high vapor pressure of silicon and perhaps suboxide formation in vacuum.

Compositions containing the other metals sintered normally, without cracking. Zirconium tends to collect at the grain boundaries in thick layers, and the structure is similar to that of vacuum hot-pressed pure zirconia (Fig. 6). Vanadium tends to behave in a similar manner.

The structures of the zirconia-chromium and hafnia-titanium compositions are similar to those of ZT-15 (Fig. 2) but with better metal distribution and less porosity because of milling of the former two mixtures.

The fact that disks of these compositions can be made at all indicates that the materials have reasonably good thermal shock resistance, otherwise they would crack on cooling through the transformation range of the matrix (just like zirconia, hafnia undergoes an allotropic transformation at about 1700°C ,¹⁹ which is below the 1870°C sintering temperature used).

Disks of the previously named compositions ground to $1\frac{3}{8}$ inch in diameter by $5/16$ inch thick were thermally shocked in boiling water by the methods described in reference 1. The results of the tests are shown in Table 3, where ΔT was obtained from the equation

$$\Delta T = \frac{T_1 + T_2}{2} - 100$$

where

T_1 maximum temperature specimen withstood without cracking, $^{\circ}\text{C}$

T_2 lowest temperature at which cracking was observed, $^{\circ}\text{C}$

The results shown in Table 3, are only approximate, since they

represent averages of two tests, and thermal shock tests usually show large scatter in the ΔT values. The results do show, however, that the theory of reference 15 that the improved thermal shock resistance of zirconia-titanium compositions is due to the substitutional solid solution of titanium in zirconia can hardly be correct, for, as shown, in Table 3, ZZ-15-M (made from zirconia and zirconium metal) has nearly the same thermal shock resistance of ZT-15-M (made from zirconia and titanium metal).

It may be pointed out that, although tungsten, molybdenum, and silicon did not appear to improve the thermal shock resistance of zirconia, it does not necessarily mean that they are unsuitable for this purpose, but perhaps rather that the techniques used were incorrect.

In another series of experiments, bodies of zirconia with 8.2 volume percent nickel and of zirconia with 8.2 volume percent of a mixture of 60 weight percent molybdenum and 40 weight percent manganese were made by hot-pressing at 1280°C , 2000 psi, for 1 hour in vacuum. The hot-pressed bodies were black (same as ZT-15-M). Although no quantitative thermal shock tests were carried out with these two compositions, the very fact that they could be cooled through the transformation range without cracking indicates that they have relatively good thermal shock resistance.

From the experiments described above, it can be concluded that titanium is by no means unique in its ability to improve the thermal shock resistance of zirconia.

IV. CONCLUDING REMARKS

From the results of the present investigation it is concluded that

1. Titanium additions inhibit the grain growth of zirconia. This accounts at least in part for the relatively high strength of the zirconia-titanium compositions and, hence, for the relatively good thermal shock resistance of zirconia-titanium compositions for quenches from below the transformation temperature of zirconia.

2. The discrepancy between calculated and experimental thermal shock resistance of zirconia with 15 mole percent titanium for quenches through the transformation range is attributed in great part to the elastoplastic behavior of these compositions through the transformation range.

3. Zirconia-zirconium cermets exhibit a similar elastoplastic behavior through the transformation range.

4. The black color of the zirconia-titanium compositions was traced to the presence of metal in the grain boundaries. Many other metals also render zirconia either metallic dark gray or black in color.

5. It is surmised that besides its grain growth inhibiting effect, titanium contributes to improvement in thermal shock resistance of zirconia by acting as a crack arrester and by allowing grain boundary sliding.

6. Other metals (chromium, zirconium, vanadium, e.g.) besides titanium can improve the thermal shock resistance of zirconia. Not all metal additions inhibit grain growth. Some, in fact, enhance grain growth (zirconium, e.g.) but in these cases the metallic grain boundary must be correspondingly thicker to prevent cracking due to thermal shock.

7. The thermal shock resistance of many other ceramics should be improved by metal additions.

8. Considering the chemical similarity of the oxides of zirconium, hafnium, and thorium, the results of this investigation should also be applicable (with only minor changes) to the two latter materials.

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TABLE 1. - CHEMICAL COMPOSITION, PARTICLE SIZE, AND SUPPLY SOURCE OF RAW MATERIALS

Material	Composition, percent	Original particle size	Method of analysis
Zirconium oxide	98.8 ZrO ₂ (includes HfO ₂), 0.33 Si, 0.10 TiO ₂ , 0.10 CaO	0.26 μ	B.E.T.
Zirconium oxide (stabilized)	92.5 ZrO ₂ (includes HfO ₂), 5.33 CaO, 0.63 MgO, 0.50 Al ₂ O ₃ , 0.37 SiO ₂		-----
Hafnium oxide	95 HfO ₂ approx.	-325 Mesh	Sieve
Titanium powder	98 Ti, 1.1 N	-325 Mesh	Sieve
Zirconium powder	98 Zr (includes 2 to 3 Hf)	-200 Mesh	Sieve
Chromium powder	99.0 Cr, min.	-300 Mesh	Sieve
Vanadium powder	99.7 V	20 Mesh	Sieve
Silicon powder	97 Si, min.	-100 Mesh	Sieve
Molybdenum powder	>99 Mo	4.5 μ	Fisher
Tungsten powder	>99.5 W	1.15 μ	Fisher

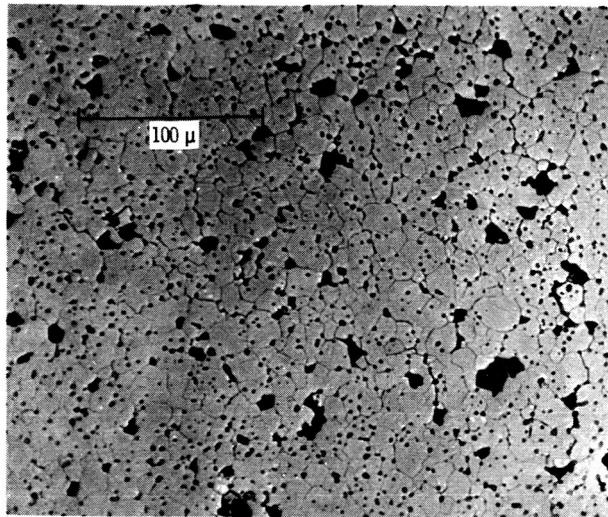
TABLE 2. - DESIGNATION, COMPOSITION, AND TREATMENT OF SAMPLES

Designa- tion	Composition	Treatment	Density, g/cc
ZT-15	Zirconia + 15 mole percent titanium	Mixed, cold-pressed, vacuum sintered at 1870° C for 1 hr	5.20 to 5.27
ZT-15-M	Zirconia + 15 mole percent titanium	Milled, cold-pressed, vacuum sintered at 1870° C for 1 hr	5.65 to 5.75
ZT-15-HP	Zirconia + 15 mole percent titanium	Mixed, and vacuum hot-pressed at 1600° C and 2000 psi for 1 hr	5.30 to 5.60
Z-0-HP	Zirconia	Vacuum hot-pressed at 2025° C and 2000 psi for 1 hr	5.81
ZZ-15-M	Zirconia + 15 mole percent zirconium	Milled, cold-pressed, and vacuum sintered at 1870° C for 1 hr	5.82
ZCr-15-M	Zirconia + 15 mole percent chromium	→ Milled, cold-pressed, and vacuum sintered at 1870° C for 1 hr	5.82
ZV-15-M	Zirconia + 15 mole percent vanadium	→ Milled, cold-pressed, and vacuum sintered at 1870° C for 1 hr	5.80
ZM-15-M	Zirconia + 15 mole percent molybdenum	→ Milled, cold-pressed, and vacuum sintered at 1870° C for 1 hr	5.80
ZS-15-M	Zirconia + 15 mole percent silicon	→ Milled, cold-pressed, and vacuum sintered at 1870° C for 1 hr	5.80
ZW-15-M	Zirconia + 15 mole percent tungsten	→ Milled, cold-pressed, and vacuum sintered at 1870° C for 1 hr	5.80
HT-15-M	Hafnia + 15 mole percent titanium	→ Milled, cold-pressed, and air sintered at 1800° C for 3 hr	9.22
EM	Calcia-stabilized zirconia (Zircos B)	→ Milled, cold-pressed, and air sintered at 1800° C for 3 hr	5.22

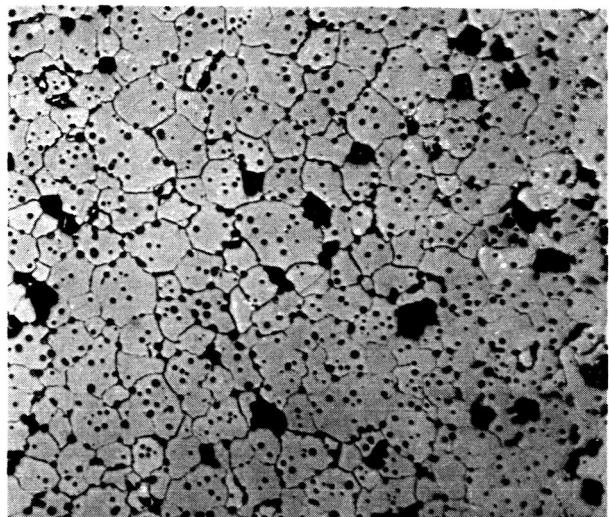
TABLE 3. - THERMAL SHOCK RESISTANCE OF VARIOUS
COMPOSITIONS QUENCHED IN BOILING WATER

Designa-tion	Composition	Thermal shock parameter, ΔT , °C
HT-15-M	Hafnia + 15 mole percent titanium	138
ZCr-15-M	Zirconia + 15 mole percent chromium	220
ZT-15-M	Zirconia + 15 mole percent titanium	350
ZV-15-M	Zirconia + 15 mole percent vanadium	81
ZZ-15-M	Zirconia + 15 mole percent zirconium	299
Z-O-HP	Zirconia	159

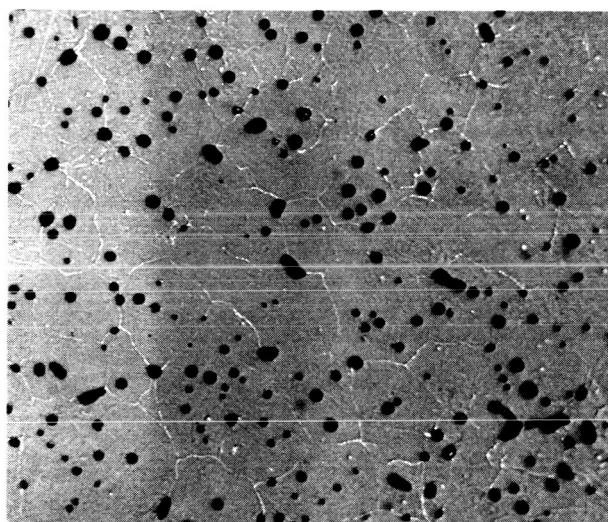
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(a) 1820° C.



(b) 1980° C.



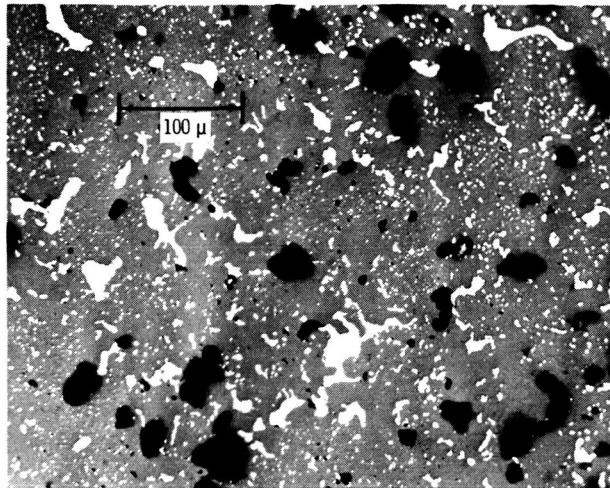
(c) 2400° C.



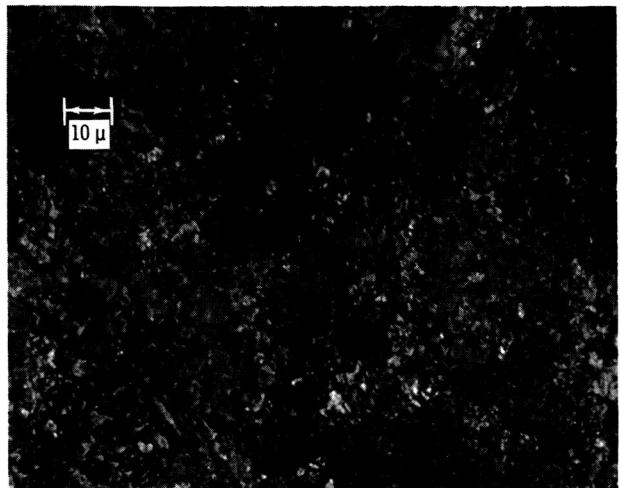
(d) 2620° C.

Figure 1. - Microstructures of pure zirconia after vacuum sintering for 1 hour at various temperatures. Unetched. X250.

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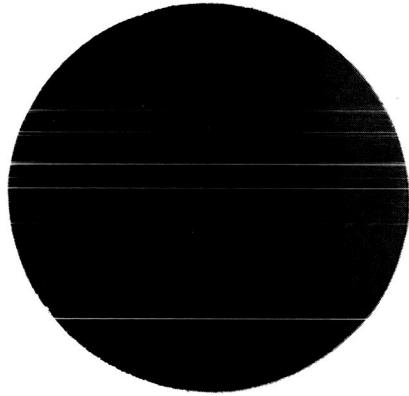
(a) Unetched.



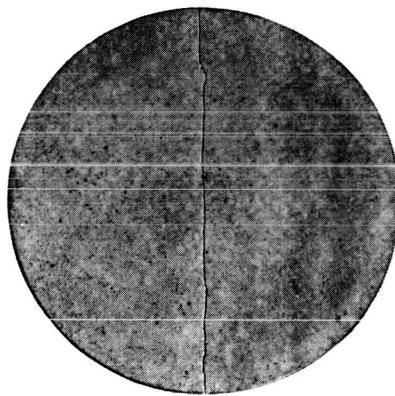
(b) Etchant, hydrofluoric acid.

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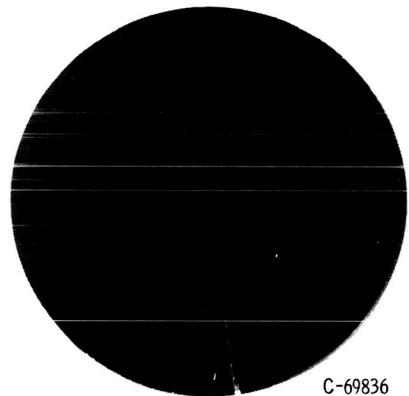
Figure 2. - Microstructure of zirconia with 15 mole percent titanium, cold-pressed, and sintered in vacuum at 1870° C for 1 hour.



(a) Milled zirconia with 15 mole percent titanium (ZT-15-M, table II) thermally shocked from below transformation temperature.



(b) Milled and air-sintered calcia-stabilized zirconia (BM, table II) thermally shocked.



(c) Milled zirconia with 15 mole percent titanium (ZT-15-M, table II) thermally shocked from above transformation temperature.

Figure 3. - Thermally shocked disks.

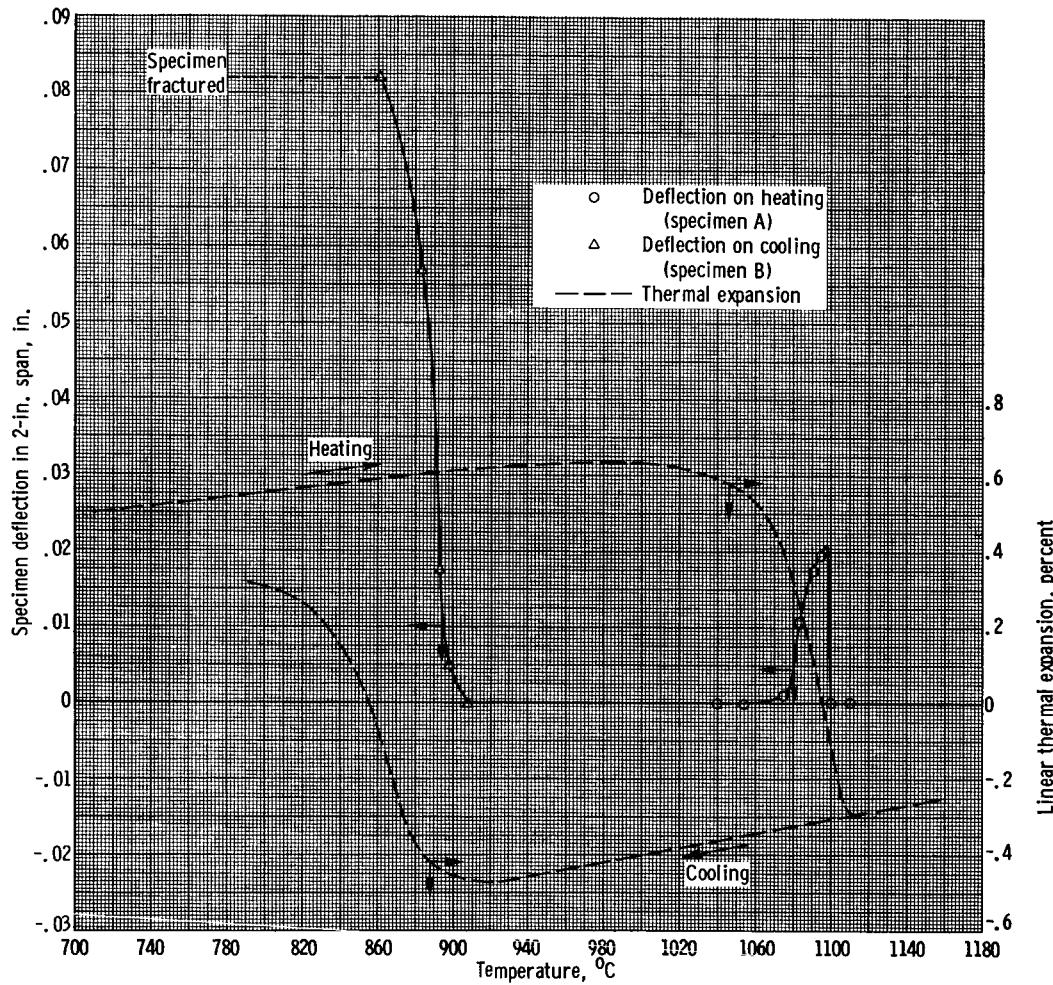


Figure 4. - Plastic deformation of zirconium oxide with 15 mole percent titanium (ZT-15-M) on heating and cooling through transformation range showing correspondence with thermal expansion curves. Specimen dimensions, 0.500 inch wide by 0.100 inch thick; maximum fiber stress, 21,000 psi; heating rate, 3.7°C per minute; cooling rate, 4.5°C per minute.

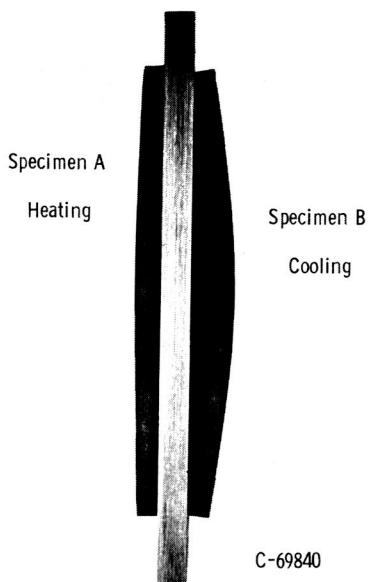


Figure 5. - Specimens of zirconia with 15 mole percent titanium (ZT-15-M) after cycling through transformation temperature. Center piece is a straight edge.

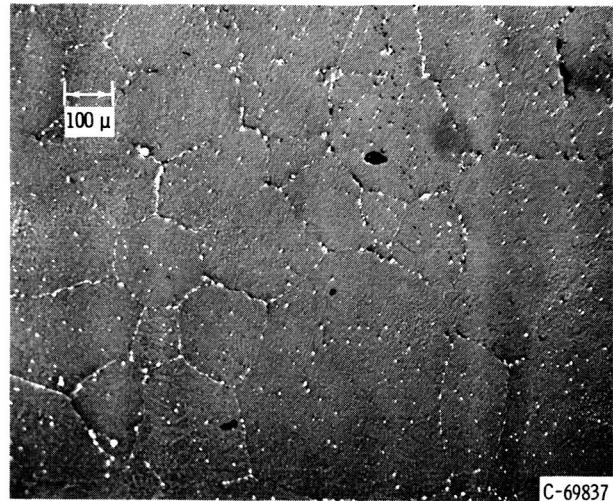


Figure 6. - Microstructure of pure zirconia after vacuum hot-pressing at 2025° C and 2000 psi for 1 hour. Unetched.

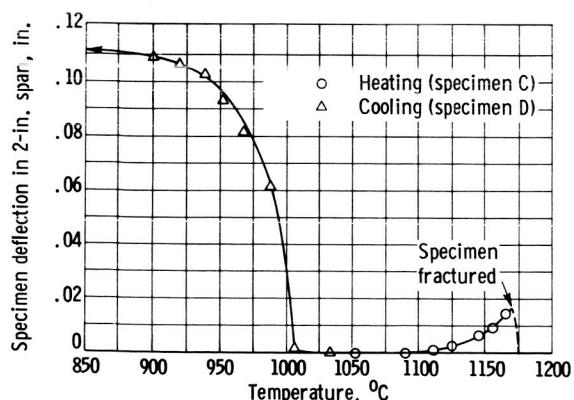


Figure 7. - Plastic deformation of vacuum hot-pressed zirconium oxide (Z-0-HP) on heating and cooling through transformation range. Specimen dimensions, 0.493 inch wide by 0.101 inch thick; maximum fiber stress, 12,000 psi; heating rate, 3.5° C per minute; cooling rate, 3.2° C per minute.

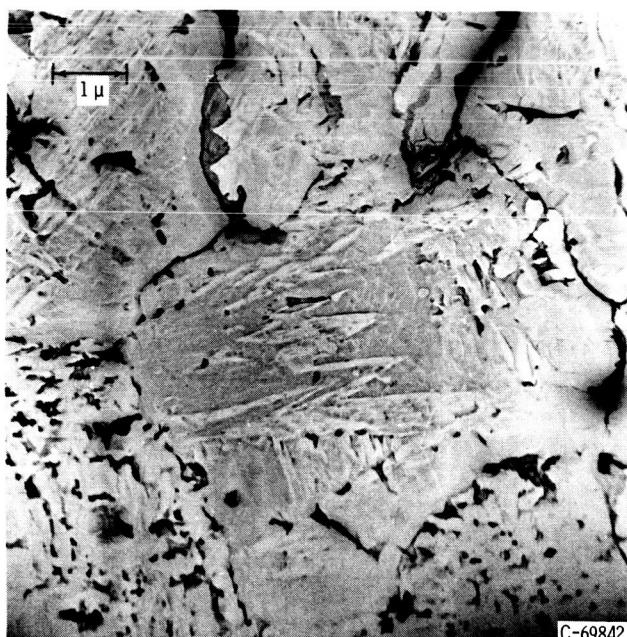


Figure 8. - Electron photomicrograph of deeply etched zirconia plus 15 mole percent titanium (ZT-15-M)